

Development of HUMASORB™, A Lignite Derived Humic Acid for Removal of Metals and Organic Contaminants from Groundwater

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Introduction¹

Heavy metal and organic contamination of surface and groundwater is a major environmental concern. The contamination is primarily due to improperly disposed industrial wastes. Decontamination of surface and groundwater can be achieved using a broad spectrum of treatment options such as precipitation, ion- exchange, microbial digestion, membrane separation, activated carbon adsorption, etc. The state-of-the-art technologies for treatment of contaminated water, however, can in one pass remediate only one class of contaminants, i.e., either VOCs (activated carbon) or heavy metals (ion exchange). The groundwater contamination at different Department of Energy (DOE) sites (e.g., Hanford) is due to the presence of both VOCs and heavy metals. Therefore, two different stepwise processes are needed to remediate a site. The two-step approach increases the cost of remediation. A novel material having properties to remove both classes of contaminants in one step is being developed as part of this project.

Objective

The objective of this project is to develop a lignite derived adsorbent, HUMASORB™, to remove heavy metal and organic contaminants from groundwater and surface water streams in one processing step. As part of this project, HUMASORB™ is being characterized and evaluated for its ion-exchange and adsorption capabilities.

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Approach

This project is aimed at the development of HUMASORB™, an adsorbent having the unique properties of humic acid. Humic acid is a natural material with many properties which can be exploited for several cost effective applications. Humic substances are complex mixtures of naturally occurring organic materials. These substances are formed from the decay of plant and animal residues in the environment. Humic acid constitutes a significant portion of the acid radicals found in humic substances.

A major source of humic acid is coal-- the most abundant and predominant product of plant residue coalification. All ranks of coal contain humic acid but lignite represents the most easily available and concentrated form of humic acid. Humic acid concentration of lignite varies from 30-90 % depending on location. Peat, humates and sewage sludge also contain significant quantities of humic acid.

The properties of humic acid for chelation of metals and adsorption of organics were reviewed in an earlier report on this project (1). As discussed in that report, humic acid is dark brown to black in color. It is considered a complex aromatic macromolecule with various linkages between the aromatic groups. The different compounds involved in linkages include, amino acids, amino sugars, peptides, aliphatic acids and other aliphatic compounds. The various functional groups in humic acid include, carboxylic (COOH), phenolic, aliphatic and enolic - hydroxyl and carbonyl (C=O) structures of various types. Humic acid is an association of molecules forming aggregates of elongated bundles of fibers at low pHs and open flexible structures perforated by voids at high pHs. The voids can trap and adsorb both organic and inorganic particles if the charges are complementary.

Project Description

This project is underway to develop HUMASORB-CS™ to remove in one processing step, heavy metal and organic contaminants from groundwater and surface waters found at typical DOE and industrial sites. The development of HUMASORB™ is divided into two phases. Phase I-- isolation, purification, and evaluation of humic acid, preparation and preliminary characterization of HUMASORB-CS™, was successfully completed and was a significant milestone and a major decision point. Under the Phase II activities, that began in April 1996, HUMASORB-CS™ was successfully cross-linked and immobilized. The new material is currently undergoing bench- and pilot-scale column tests. The various tasks in Phase I included:

- isolation and purification of humic acid
- characterization of contaminant removal
- cross-linking humic acid to form HUMASORB-CS™
- evaluation of HUMASORB-CS™ for contaminant removal

The tasks in Phase II include:

- immobilization of HUMASORB-CSTM to improve handling properties and lower solubility
- evaluation of immobilized HUMASORB-CSTM in batch and column studies
- stability studies on HUMASORB-CSTM
- conceptual process design and economic analysis.

The procedure for the experiments used to determine contaminant removal in batch mode are presented elsewhere (1). A similar procedure was used for the experiments from which the results are presented here. The humic acid based adsorbents used in this project include:

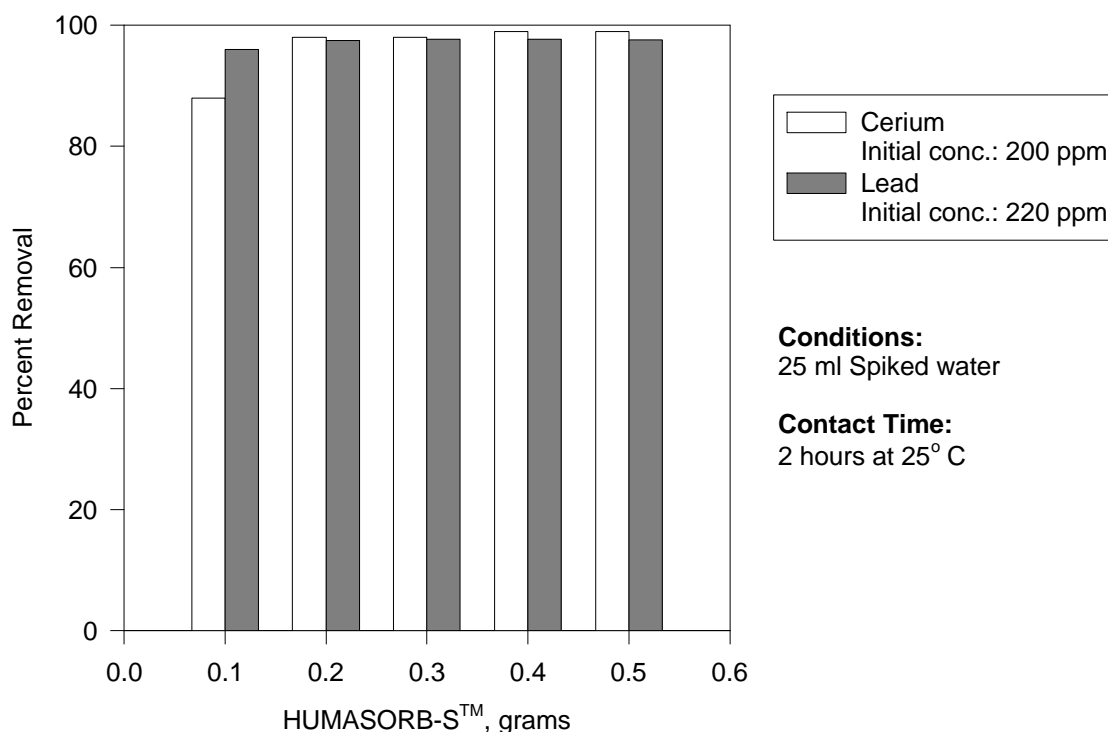
- liquid humic acid termed HUMASORB-LTM
- purified humic acid termed HUMASORB-STM
- cross-linked humic acid obtained from either HUMASORB-LTM or HUMASORB-STM termed HUMASORB-CSTM

Results

The effectiveness of HUMASORBTM for removal of different metals, organics and representative radionuclides was presented earlier (1). The metal-sorption data was analyzed using the method developed by Scatchard (2). The presence of more than one inflection point on a plot based on Scatchard analysis usually indicates the presence of more than one type of binding site. Scatchard analysis of the results from the experiments in this study indicated the possibility of more than one type of binding site for copper and nickel sorption. The plot was however, linear for cadmium indicating that possibly only one type of binding site was active for cadmium sorption (1).

The effect of HUMASORB-STM loading on removal of lead and cerium (a surrogate for plutonium) from simulated waste streams is shown in Figure 1. The results indicate that HUMASORBTM has high affinity for both lead and cerium. The mechanism for contaminant removal is believed to be a combination of ion-exchange and chelation/complexation. The results presented in Figure 1 are with simulated waste streams containing only one contaminant. The effect of multiple contaminants on HUMASORB-STM performance was evaluated using a simulated waste stream containing copper, chromium and lead and treating it with HUMASORB-STM at different loadings. The effect of contact time was also evaluated by reacting for two hours and 24 hours. The results indicate a relatively higher affinity for lead and copper removal compared to that for chromium (Figure 2). In addition, increased contact time did not have any significant effect on the removal of lead and copper. However, the removal of chromium increased with longer contact time and chromium removal was relatively lower compared to lead

Figure 1. HUMASORB-STM is Effective for Metal Removal



and copper for a given adsorbent loading. This indicates that the removal of chromium could be the rate limiting step under the conditions of this study.

HUMASORB-STM is insoluble in water at lower pH, but could dissolve at higher pH in the presence of monovalent metals ions such as sodium and potassium. A cross-linked humic acid polymer--HUMASORB-CSTM was produced to overcome this limitation and lower the solubility at higher pHs. HUMASORB-CSTM was produced by cross-linking HUMASORB-S/LTM using different proprietary methods. The solubility of the cross-linked product was determined at various pH and compared with humic acid. The results shown in Figure 3 indicate that the solubility of HUMASORB-CSTM, as determined under the conditions of this study, is significantly lower compared to that of humic acid. The different functional groups present in HUMASORBTM before and after cross-linking were estimated using ¹³C-NMR and are shown in Table 1. The analysis indicates that all the functional groups, that are believed to be responsible for contaminant removal, are retained after cross-linking.

The ability of HUMASORB-CSTM to remove different contaminants was evaluated and compared with removal before cross-linking. The results from simulated streams containing single contaminants such as chromium, strontium (Figures 4 & 5) and streams containing multiple contaminants such as copper, chromium and lead (Figure 6) indicate that the contaminant removal properties of humic acid are retained in HUMASORB-CSTM and in a few cases enhanced after

cross-linking. In addition, the results with a stream containing multiple contaminants, indicate that chromium removal is the rate limiting step and required higher loading of the adsorbent. This is similar to the performance of HUMASORB™ before cross-linking.

Figure 2. HUMASORB-S™ is Effective for Metal Removal from Simulated Waste Streams Containing Multiple Contaminants

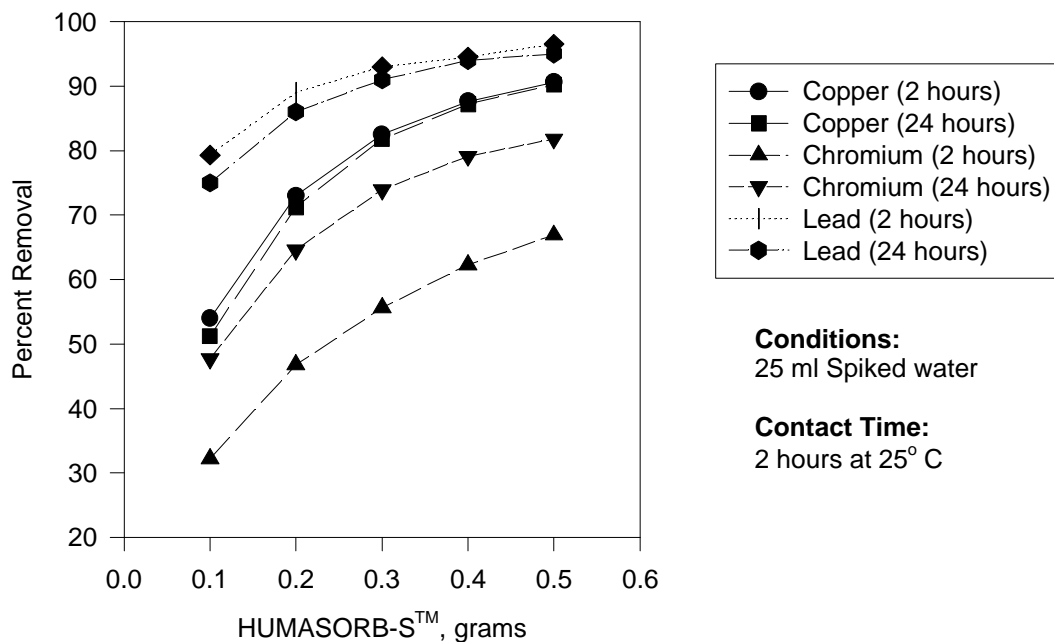


Table 1

FUNCTIONAL GROUP COMPOSITION OF DIFFERENT HUMASORB-CS™ PRODUCTS
(ESTIMATED FROM SOLID STATE ¹³C-NMR SPECTROSCOPY)

SAMPLE	Paraffinic carbon, amines %	Carbohydrates, alcohols %	Aromatic carbon %	Carboxyl %
HUMASORB-L™ (dried)	8.84	15.01	57.96	18.14
HUMASORB-S™	21.94	23.75	37.03	17.24
HUMASORB-CS™ (enzymatically)	26.39	21.87	33.58	18.11
HUMASORB-CS™ (chemically)	22.98	26.22	34.05	16.69

Figure 3: HUMASORB-CS™ Solubility is Lower After Cross-Linking and Immobilization

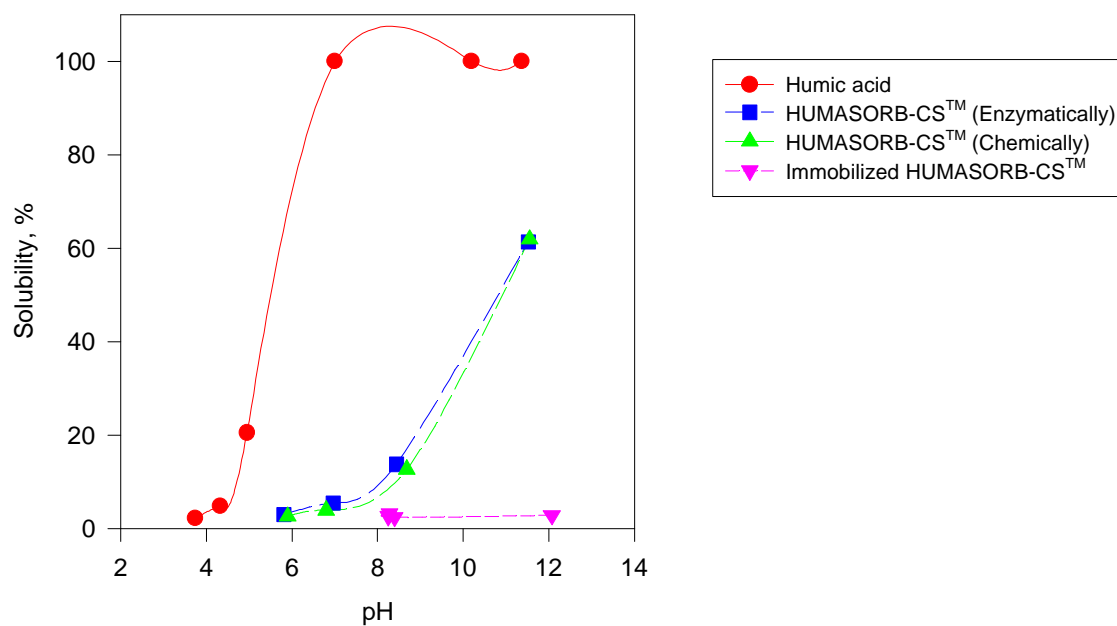


Figure 4: Chromium (III) Removal is Significantly Enhanced by HUMASORB-CS™

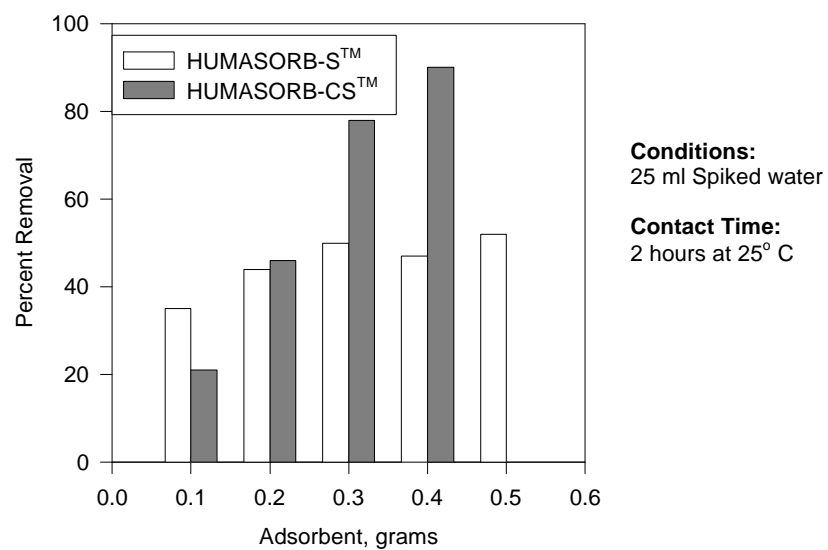


Figure 5: HUMASORB-CS™ Enhances Strontium Removal

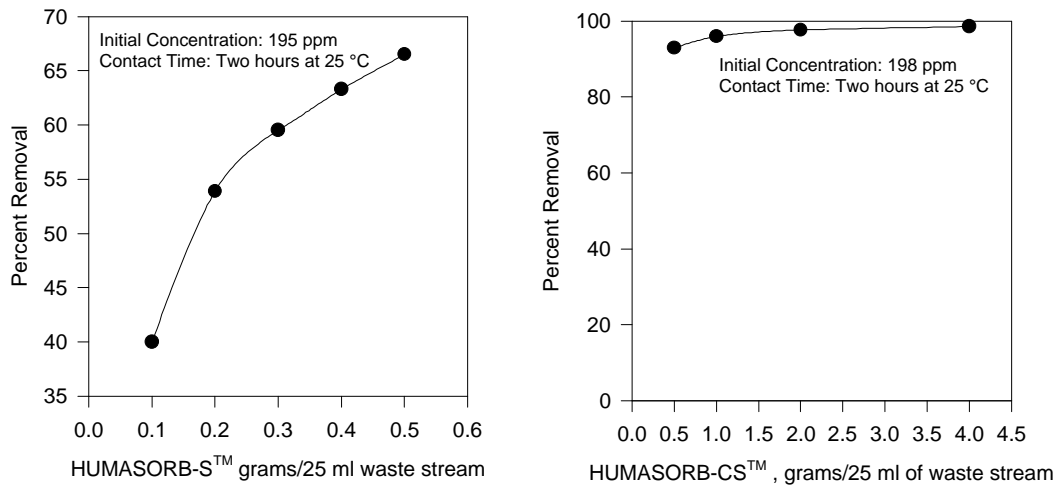
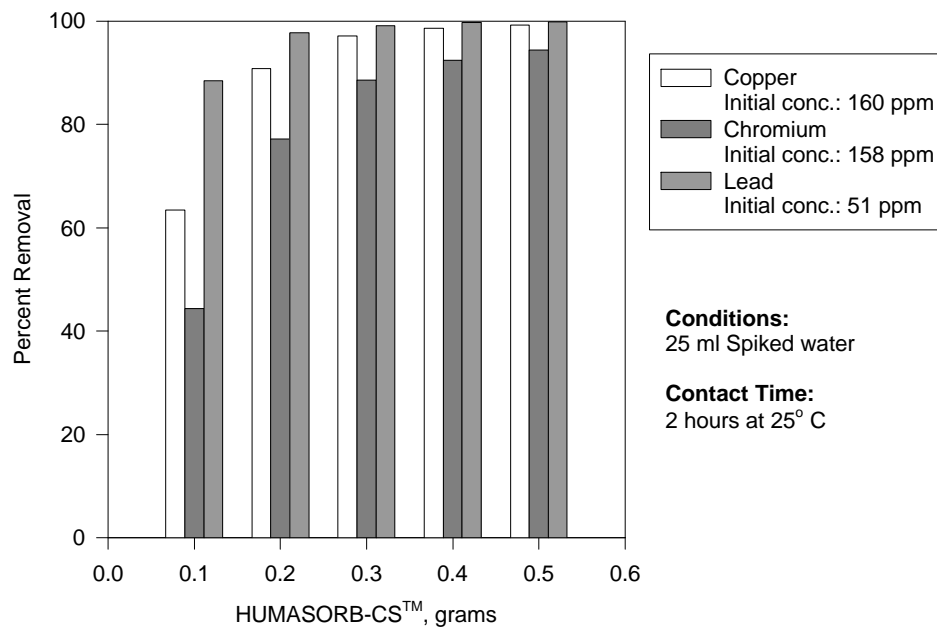


Figure 6: Multiple Toxic Metal Removal from Spiked Water by HUMASORB™



The results from some of the experiments conducted as part of this project were used to determine the distribution coefficients. The coefficient K_d is defined as

$$K_d \equiv C_s / C_l$$

where, C_s is the concentration of the contaminant in the solid phase and C_l is the concentration in the liquid phase.

Distribution coefficients for various contaminants are listed in Tables 2 & 3. The distribution coefficient was determined from batch isotherm studies, in which different amounts of the adsorbent were contacted with simulated waste streams. The table indicates that HUMASORB-S™ has very high affinity for uranium, and is also very effective in removing different metals from simulated waste streams.

The data presented in Tables 2 & 3 indicate that HUMASORB™ had higher distribution coefficients after cross-linking. The higher distribution coefficients with HUMASORB-CS™ at comparatively lower equilibrium concentration indicates that cross-linking has enhanced metal removal from contaminated water. Higher distribution coefficients with HUMASORB-CS™ for different metals is also evident in batch adsorption studies with contaminated streams containing multiple metals as shown in Table 3.

Table 2: HUMASORB-CS™ Enhances Strontium and Chromium Distribution Coefficients

CONTAMINANT	EQUILIBRIUM CONCENTRATION IN THE LIQUID PHASE, ppm	DISTRIBUTION COEFFICIENT*, K_d , ml/gm	pH
WITH HUMASORB-S™			
Uranium	0.01	> 100,000	5.1
Lead	5	3500	2.25
Cerium	1.7	5600	2.5
Strontium	65.3	99	2.2
Chromium	138	54	3.2
WITH HUMASORB-CS™			
Strontium	2.87	430	5.1
Chromium	22.65	566	3.2

*: As determined from batch isotherm studies with only one contaminant present in the system.

Column Studies: HUMASORB-CS™ is now being used in bench-scale columns in continuous mode. In these studies, simulated waste streams containing various contaminants are passed through a column packed with HUMASORB-CS™ or a mixture of sand and HUMASORB-CS™. The empty bed contact time (EBCT) in most of the studies conducted to date range from one to four minutes. In one of the experiments, EBCT was approximately 13 minutes. The bed volumes treated at breakthrough depends on the contaminant and its concentration in the input stream to the column. In one of the column studies, breakthrough was not attained even after 2500 bed volumes based on HUMASORB-CS™ loading in the column. A detailed analysis of the results from the column studies conducted to date is underway at present. The spent HUMASORB-CS™ from the column studies was regenerated by traditional techniques used to regenerate ion-exchange resins. The results show that HUMASORB-CS™ could be regenerated for at least one or two cycles.

Table 3: HUMASORB-CS™ Enhances Copper, Chromium, and Lead Distribution Coefficients

CONTAMINANT	EQUILIBRIUM CONCENTRATION IN THE LIQUID PHASE, ppm	DISTRIBUTION COEFFICIENT*, K_d , ml/gm	pH
WITH HUMASORB-S™			
Copper	6.8	666	2.2
Chromium	14	260	2.2
Lead	2	450	2.2
WITH HUMASORB-CS™			
Copper	< 0.5	11,870	4.0
Chromium	< 0.5	8514	4.0
Lead	< 0.5	1700	4.0

*: As determined from batch isotherm studies with three inorganic and two organic contaminants present in the system.

Future work

HUMASORB-CS™ developed in this study will be used in column studies using various representative contaminants. The types of contaminants to be evaluated during Phase II of this project include metal ions, radionuclides or surrogates, oxo-anions, chlorinated and fuel hydrocarbons. The future work in this project includes:

- evaluation of contaminant removal in columns packed with HUMASORB-CS™,
- evaluate stability of HUMASORB-CS™ in water at different temperatures, and in the presence of ions such as carbonate, sulfate,
- conceptual design and economic analysis.

Applications/Benefits

The remediation of contaminated streams and groundwater has been traditionally approached with at least a two-step process including some combination of activated carbon and ion-exchange process. HUMASORB-CS™, derived from a naturally occurring material has the potential to alleviate some of the limitations of multi-step processing by combining remediation efforts into a single step process. The use of a single-step process for remediation systems could reduce the cost of clean-up of various contaminated streams and groundwater at a number of DOE facilities. HUMASORB-CS™ can be used for groundwater clean-up both in the in-situ mode and in a pump and treat process. The benefits of HUMASORB-CS™ use include:

- Improved process performance due to enhanced contaminant removal by HUMASORB-CS™

- Reduced unit operations obviating the need for multiple process units
- Reduced complexity of metal-recovery and waste disposal when needed.

Acknowledgments

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References

1. Sanjay, H.G., et al. In Proceedings of the Environmental Technology Through Industry Partnership Conference, October 1995, DOE/METC-96/1021, Vol. 2.
2. Scatchard, G. The attraction of proteins for small molecules and ions, Ann. New York Acad. Sci., 51, 660-672, 1949.